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10 DEC 1998

FORM-PTO-1390 (Rev. 10-96)		U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE		ATTORNEY'S DOCKET NUMBER 022701-803	
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371				U.S. APPLICATION NO. (If known, see 37 C.F.R. 1.5) <div style="font-size: 24pt; font-weight: bold; text-align: center;">09/202244</div>	
INTERNATIONAL APPLICATION NO. PCT/FR97/01055		INTERNATIONAL FILING DATE 12 June 1997		PRIORITY DATE CLAIMED 12 June 1996	
TITLE OF INVENTION METHOD FOR PREPARING SILICONE OILS BY HYDROSILYLATION WITH POLYORGANOHYDROGENOSILOXANES AND UNITS CONTAINING AT LEAST ONE HYDROCARBON RING INCLUDING AN OXYGEN ATOM, IN THE PRESENCE OF A HETEROGENEOUS CATALYTIC COMPOSITION					
APPLICANT(S) FOR DO/EO/US Stefan BREUNIG; Gérard MIGNANI					
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:					
1. <input checked="" type="checkbox"/> This is a FIRST submission of items concerning a filing under 35 U.S.C. 371.					
2. <input type="checkbox"/> This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371.					
3. <input checked="" type="checkbox"/> This is an express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and the PCT Articles 22 and 39(1).					
4. <input checked="" type="checkbox"/> A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.					
<input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371(c)(2))					
a. <input checked="" type="checkbox"/> is transmitted herewith (required only if not transmitted by the International Bureau).					
b. <input checked="" type="checkbox"/> has been transmitted by the International Bureau.					
c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US)					
<input checked="" type="checkbox"/> A translation of the International Application into English (35 U.S.C. 371(c)(2)).					
<input type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))					
a. <input type="checkbox"/> are transmitted herewith (required only if not transmitted by the International Bureau).					
b. <input type="checkbox"/> have been transmitted by the International Bureau.					
c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired.					
d. <input type="checkbox"/> have not been made and will not be made.					
8. <input type="checkbox"/> A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).					
9. <input type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).					
10. <input type="checkbox"/> A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).					
Items 11. to 16. below concern other document(s) or information included:					
11. <input checked="" type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98.					
12. <input type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.					
13. <input checked="" type="checkbox"/> A FIRST preliminary amendment.					
<input type="checkbox"/> A SECOND or SUBSEQUENT preliminary amendment.					
14. <input type="checkbox"/> A substitute specification.					
15. <input type="checkbox"/> A change of power of attorney and/or address letter.					
16. <input type="checkbox"/> Other items or information:					

17. ☒ The following fees are submitted:

CALCULATIONS

PTO USE ONLY

Basic National Fee (37 CFR 1.492(a)(1)-(5)):

Search Report has been prepared by the EPO or JPO \$840.00

International preliminary examination fee paid to USPTO (37 CFR 1.482) \$670.00

No international preliminary examination fee paid to USPTO (37 CFR 1.482)
but international search fee paid to USPTO (37 CFR 1.445(a)(2)) \$760.00Neither international preliminary examination fee (37 CFR 1.482) nor
international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$970.00International preliminary examination fee paid to USPTO (37 CFR 1.482)
and all claims satisfied provisions of PCT Article 33(2)-(4) \$96.00**ENTER APPROPRIATE BASIC FEE AMOUNT =**

\$ 840.00

Surcharge of \$130.00 for furnishing the oath or declaration later than
months from the earliest claimed priority date (37 CFR 1.492(e)).☐ 20 ☐ 30

\$

Claims

Number Filed

Number Extra

Rate

Total Claims

21 -20 =

1

X\$18.00

\$ 18.00

Independent Claims

2 -3 =

0

X\$78.00

\$ --

Multiple dependent claim(s) (if applicable)

+ \$260.00

\$

TOTAL OF ABOVE CALCULATIONS =

\$ 858.00

Reduction for 1/2 for filing by small entity, if applicable. Verified Small Entity statement must also be
filed. (Note 37 CFR 1.9, 1.27, 1.28).

\$

SUBTOTAL =

\$ 858.00

Processing fee of \$130.00 for furnishing the English translation later than
months from the earliest claimed priority date (37 CFR 1.492(f)).☐ 20 ☐ 30

\$

TOTAL NATIONAL FEE =

\$ 858.00

Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied
by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property +

\$

TOTAL FEES ENCLOSED =

\$ 858.00

Amount to be:
refunded

\$

charged

\$

a. ☒ A check in the amount of \$ 858.00 to cover the above fees is enclosed.b. ☐ Please charge my Deposit Account No. 02-4800 in the amount of \$ to cover the above fees. A duplicate copy of this sheet
is enclosed.c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit
Account No. 02-4800. A duplicate copy of this sheet is enclosed.**NOTE:** Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be
filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

Norman H. Stepno
BURNS, DOANE, SWECKER & MATHIS, L.L.P.
P.O. Box 1404
Alexandria, Virginia 22313-1404

SIGNATURE

Teresa Stanek Rea

NAME

30,427

REGISTRATION NUMBER

09/202244
300 Rec'd PCT/PTO 10 DEC 1998

Patent
Attorney's Docket No. 022701-803

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of)
Stefan BREUNIG et al) Group Art Unit: Unassigned
Application No.: Unassigned) Examiner: Unassigned
(Corresponds to PCT/FR97/01055)
International Filing Date: 12 June 1997
For: METHOD FOR PREPARING SILICONE
OILS BY HYDROSILYLATION WITH
POLYORGANOHYDROGENOSILOXANES
AND UNITS CONTAINING AT LEAST
ONE HYDROCARBON RING INCLUDING
AN OXYGEN ATOM, IN THE PRESENCE
OF A HETEROGENEOUS CATALYTIC
COMPOSITION)

PRELIMINARY AMENDMENT

BOX PCT

Assistant Commissioner for Patents
Washington, D.C. 20231

Sir:

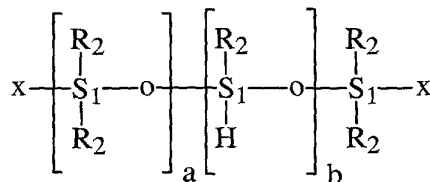
Prior to examination, please amend the above-captioned application as follows:

IN THE CLAIMS:

Kindly amend the claims as follows:

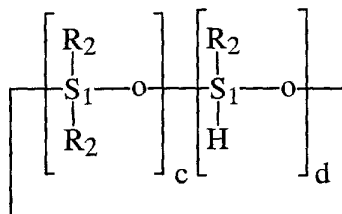
1. (Amended) Process for the preparation of a nonturbid functionalized silicone oil of stable viscosity by hydrosilylation of a polyorganohydrosiloxane with synthons [, characterized in that] wherein:

- (1) the synthons hydrosilylated with the polyorganohydrosiloxane are different or identical, comprising at least one hydrocarbon-comprising ring in which is included at least one oxygen atom,
- (2) [the] said hydrosilylation reaction is carried out in the presence of a heterogeneous catalytic composition comprising a metal [chosen from the group consisting of] comprising cobalt, rhodium, ruthenium, platinum [and] or nickel deposited on an inert support, [the] said inert support [being selected from the group consisting of] comprising carbon black, charcoal, alumina, silicate [and] or barium oxide, and
- (3) the polyorganohydrosiloxane is linear or cyclic and has the mean formulae:



(XVI)

and/or



(XVII)

in which:

- the symbols R₂ are identical or different and correspond to a monovalent hydrocarbon-comprising radical chosen from the phenyl radical and linear or

branched alkyl radicals having from 1 to 6 carbon atoms[, preferably 1 to 3 carbon atoms];

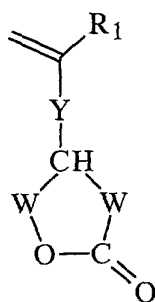
- the symbols x are identical or different and correspond to a monovalent radical chosen from R_2 , a hydrogen atom, a methoxy radical and an ethoxy radical;
- a and b are integers or fractions, such that:
 - $0 < a \leq 200$ [, preferably $0 < a \leq 99$],
 - $0 \leq b < 200$ [, preferably $1 < b \leq 100$],
 - and at least one of the two X groups corresponds to the hydrogen radical if $b = 0$,
 - $5 < a + b \leq 200$ [, preferably $10 < a + b \leq 100$];
- c and d are integers or fractions, such that:
 - $0 < c < 5$, [preferably $0 < c < 3$,]
 - $1 < d < 10$, [preferably $1 < d < 5$,]
 - $3 < a + b < 10$, [preferably $3 < a + b < 5$].

Claim 2, line 2: change "characterized in that" to --wherein--;

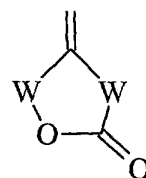
line 3: change "colourless" to --colorless--.

3. (Amended) Process according to claim 1[or 2], [characterized in that] wherein the synthons comprise at least one hydrocarbon-comprising ring in which is included an oxygen atom, the synthons having the formula:

■ (1)



and/or

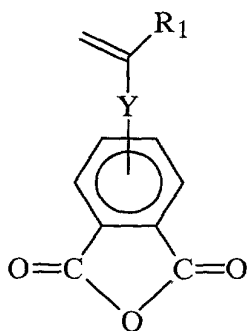


(II)

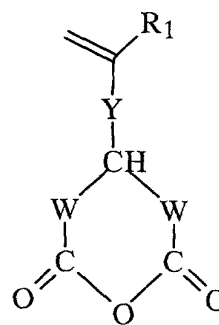
in which:

- the symbols W are identical or different and correspond to a divalent hydrocarbon-comprising radical [chosen from] comprising linear or branched alkylene radicals having from 1 to 12 carbon atoms, it being possible for one of the symbols W to be a free valency;
- the symbol Y corresponds to a free valency or a divalent radical [chosen from] comprising linear or branched alkylene radicals having from 1 to 12 carbon atoms which can comprise a heteroatom[, preferably an oxygen atom];
- the symbol R₁ corresponds to a hydrogen atom or monovalent hydrocarbon-comprising radical [chosen from] comprising linear or branched alkyl radicals having from 1 to 12 carbon atoms[and preferably a hydrogen atom or a methyl radical];

■ (2)



(III)



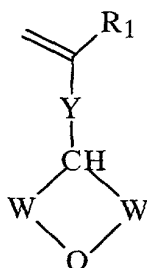
and/or

(IV)

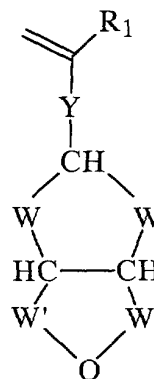
in which:

- the symbols W are identical or different and correspond to a divalent hydrocarbon-comprising radical [chosen from] comprising linear or branched alkylene radicals having from 1 to 12 carbon atoms, it being possible for one of the symbols W to be a free valency;
- the symbol Y corresponds to a free valency or a divalent radical [chosen from] comprising linear or branched alkylene radicals having from 1 to 12 carbon atoms which can comprise a heteroatom[, preferably an oxygen atom];
- the symbol R₁ corresponds to a hydrogen atom or monovalent hydrocarbon-comprising radical [chosen from] comprising linear or branched alkyl radicals having from 1 to 12 carbon atoms [and preferably a hydrogen atom or a methyl radical];

■ (3)



(V)



(VI)

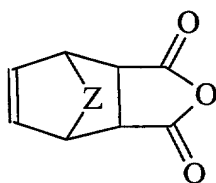
and/or

in which:

- the symbols W are identical or different and correspond to a divalent hydrocarbon-comprising radical [chosen from] comprising linear or branched alkylene radicals having from 1 to 12 carbon atoms which can comprise at least one hydroxyl functional group, it being possible for one of the symbols W to be a free valency for (V) and it being possible for both symbols W simultaneously to be a free valency for (VI);
- the symbols W' are identical or different and correspond to a divalent hydrocarbon-comprising radical [chosen from] comprising linear or branched alkylene radicals having from 1 to 12 carbon atoms, it being possible for at least one of the symbols W' to be a free valency;
- the symbol Y corresponds to a free valency or a divalent radical chosen from linear or branched alkylene radicals having from 1 to 12 carbon atoms which can comprise a heteroatom[, preferably an oxygen atom];

- the symbol R_1 corresponds to a hydrogen atom or monovalent hydrocarbon-comprising radical [chosen from] comprising linear or branched alkyl radicals having from 1 to 12 carbon atoms [and preferably a hydrogen atom or d methyl radical]; and

■ (4)



(VII)

in which:

- the symbols W are identical or different and correspond to a free valency or a divalent hydrocarbon-comprising radical [chosen from] comprising linear or branched alkylene radicals having from 1 to 2 carbon atoms;
- the symbol Z corresponds to a divalent radical [chosen from] comprising a carbon atom or a heteroatom.

Claim 4, line 2: change "characterized in that" to --wherein--;

line 3: after "in" delete "the".

Claim 5, lines 1-2: change "either one of claims 3 and 4" to --claim 3--;

line 2: change "characterized in that" to --wherein--.

Claim 6, lines 1-2: change "any one of claims 3, 4 and 5" to --claim 3--;

line 2: change "characterized in that" to --wherein--.

Claim 7, lines 1-2: change "any one of claims 3 to 6" to --claim 3--;

line 2: change "characterized in that" to --wherein--.

Claim 8, lines 1-2: change "any one of claims 1 to 7" to --claim 1--;

line 2: change "characterized in that" to --wherein--;

lines 3-4: delete ", preferably between 0.1 and 10".

Claim 9, lines 1-2: change "either one of claims 1 and 2" to --claim 1--;

line 2: change "characterized in that" to --wherein--.

Claim 10, lines 1-2: change "either one of claims 1 and 2" to --claim 1--;

line 2: change "characterized in that" to --wherein--.

Claim 11, lines 1-2: change "either one of claims 1 and 2" to --claim 1--;

line 2: change "characterized in that" to --wherein--.

Claim 12, lines 1-2: change "any one of the preceding claims" to --claim 1--;

line 2: change "characterized in that" to --wherein--.

Claim 13, lines 2-3: change "in which is included" to --having--;

line 4: change "any one of claims 1 to 12" to --claim 1--.

Claim 14, line 3: change "any one of claims 1 to 12" to --claim 1--.

Claim 15, line 3: change "any one of claims 1 to 12" to --claim 1--.

16. (Amended) [Use of the silicone oils according to any one of claims 13, 14 and 15 in the] A process for the preparation of antiadhesion products for paper, glass, plastic and/or metal comprising using the silicone oil according to claim 13.

17. (Amended) [Use of the silicone oils according to any one of claims 13, 14 and 15 in the] A process of the preparation of varnishes, inks and/or coatings comprising using the silicone oil according to claim 13.

18. (Amended) Process according to [any one of claims 1 to 12] claim 1, [characterized in that it comprises] comprising the following stages:

- (a) introducing an amount of 5 to 5000 ppm[, preferably of 10 to 100 ppm,] of heterogeneous catalytic composition with respect to the total mass of the reactants [is introduced] under an inert gas into the reaction mixture;
- (b) introducing the synthon [is introduced] into the reaction mixture;

- (c) [the] heating said mixture [is heated] to a temperature of between 25°C and 200°C [and preferably between 50°C and 160°C];
- (d) subsequently introducing the polyorganohydrosiloxane [is subsequently introduced] over a period of time of between 0 and 24 hours, [preferably between 2.5 and 5 hours,] the synthon/polyorganohydrosiloxane molar ratio being between 1 and 1.10;
- (e) filtering the reaction mass [is subsequently filtered] in order to separate the heterogeneous catalytic composition and the functionalized silicone oil; and
- (f) finally devolatilizing the functionalized silicone oil [is finally devolatilized].

Claim 19, line 2: change "characterized in that" to --wherein--.

20. (Amended) [Use of a supported heterogeneous catalytic composition in] A process for the preparation of functionalized silicone oils which are stable and nonturbid, [characterized in that the] comprising using a heterogeneous catalytic composition [comprises] a metal [chosen from the group consisting of] comprising cobalt, rhodium, ruthenium, platinum [and] or nickel deposited on an inert support, [the] said inert support [being selected from the group consisting of] comprising carbon black, charcoal, alumina, silicate [and] or barium oxide[and preferably carbon black].

21. (Amended) [Use] The process according to claim 20 [in the preparation of functionalized silicone oils which are stable, non-coloured and nonturbid], [characterized in that] wherein the inert support of the heterogeneous catalytic composition is carbon black.

REMARKS

Entry of the foregoing amendment(s) is respectfully requested.

The claims have been amended to eliminate multiple dependency and to place them in better condition for U.S. patent practice.

Should the Examiner have any questions concerning the subject application, a telephone call to the undersigned would be appreciated.

Respectfully submitted,

BURNS, DOANE, SWECKER & MATHIS, L.L.P.

By: 

Teresa Stanek Rea
Registration No. 30,427

P.O. Box 1404
Alexandria, Virginia 22313-1404
(703) 836-6620

Date: December 10, 1998

PROCESS FOR THE PREPARATION OF SILICONE OILS BY
HYDROSILYLATION WITH POLYORGANOHYDROSILOXANES AND UNITS
COMPRISING AT LEAST ONE HYDROCARBON-COMPRISING RING IN
WHICH IS INCLUDED AN OXYGEN ATOM IN THE PRESENCE OF A
HETEROGENEOUS CATALYTIC COMPOSITION

The subject-matter of the invention is a process for the preparation of silicone oils which are weakly coloured and low in turbidity by hydrosilylation of polyorganohydrosiloxanes with different or identical synthons comprising at least one hydrocarbon-comprising ring in which is included an oxygen atom, the said reaction being carried out in the presence of a heterogeneous catalytic composition comprising a metal chosen from the group consisting of cobalt, rhodium, ruthenium, platinum and nickel deposited on an inert support.

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PROCESS FOR THE PREPARATION OF SILICONE OILS BY
 HYDROSILYLATION WITH POLYORGANOHYDROSILOXANES AND UNITS
 COMPRISING AT LEAST ONE HYDROCARBON-COMPRISING RING IN
 WHICH IS INCLUDED AN OXYGEN ATOM IN THE PRESENCE OF A
 5 HETEROGENEOUS CATALYTIC COMPOSITION

The present invention relates to a novel
 process for the preparation of functionalized silicone
 oils comprising at least one hydrocarbon-comprising
 10 ring in which is included an oxygen atom. In
 particular, a subject-matter of the present invention
 is a process for hydrosilylation between
 polyorganohydrosiloxanes and unsaturated units
 comprising at least one hydrocarbon-comprising ring in
 15 which is included an oxygen atom.

Reactions between polyorganohydrosiloxanes
 and olefins or acetylenic hydrocarbons are very well-
 known. The polyorganohydrosiloxanes are, for example,
 of formulae:

- 20 - $\text{Me}_3\text{SiO}-(\text{MeHSiO})_n-(\text{Me}_2\text{SiO})_m-\text{SiMe}_3$, in
 which n and m are integers or fractions
 such that $1 \leq n \leq 1000$ and $0 < m \leq 1000$;
 - $\text{Me}_2\text{HSiO}-(\text{MeHSiO})_o-(\text{Me}_2\text{SiO})_p-\text{SiHMe}_2$, in
 which o and p are integers or fractions
 25 such that $0 < o \leq 1000$ and $0 < p \leq 1000$.

Numerous synthons can functionalize
 polyorganohydrosiloxanes; for example, alkenes,

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styrenes, allyl alcohols, allyloxy ethers or allylamines are used as synthons.

These reactions are very commonly used for the synthesis of functionalized silicone oils and the oils obtained have applications in highly varied fields, such as antiadhesion or lubrication.

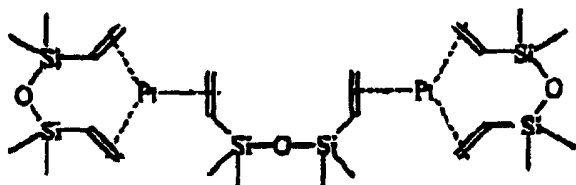
Functionalized oils can in particular be prepared with 1,2-epoxy-4-vinylcyclohexane synthons. By way of application, these functionalized silicone oils are subsequently thermally crosslinked in the presence of an acidic catalyst, such as hydrochloric acid or sulphuric acid, or photochemically crosslinked in the presence, for example, of a cationic photoinitiator, for the preparation of antiadhesive films for paper and/or plastics.

A very large number of catalytic compositions are used in hydrosilylation reactions. The most well-known catalytic compositions comprise metals, such as platinum, rhodium, cobalt or palladium. Specific examples of such catalytic compositions are platinum halides and rhodium halides, for example H_2PtCl_6 , $PtCl_2$, $(RhCl_3 \cdot xH_2O)$, complexes of platinum with siloxanes having unsaturated groups, complexes of platinum with olefins and cationic complexes of platinum with nitriles as ligands.

The catalytic compositions used in the hydrosilylation reaction are generally homogeneous

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catalytic compositions, i.e. the said compositions are dissolved in the reaction mixture. One of the most widely employed is the Karstedt catalytic composition disclosed in particular in Patent US 3,775,452; this
 5 Karstedt composition is composed of platinum complexes, the platinum having a formal and true degree of oxidation of zero (0), with the formula:



However, during the hydrosilylation reaction
 10 according to the processes of the prior art, isomerization reactions are observed, to varying degrees, within the unsaturated synthons, which requires operating with a molar excess of synthon with respect to the polyorganohydrosiloxane in the reaction
 15 mixture. This proportionate excess of synthon leads to an additional cost in the industrial implementation of the process. It would thus be desirable to reduce the necessary proportion of synthon, which would be reflected by a not insignificant saving with regard to
 20 the process:

In addition, the hydrosilylation processes of the prior art are not or not very suited to hydrosilylation reactions between polyorganohydrosiloxanes and synthons comprising a ring
 25 in which is included an oxygen atom (epoxide, and the

like). The latter, during the devolatilization stage, has a tendency to open and to cause uncontrolled polymerization and crosslinking reactions (formation of gum and/or of resin) of the functionalized oils which
5 are initiated by the presence of traces of the usual catalytic compositions, such as homogeneous catalytic compositions, which also catalyse the polymerization of rings including an oxygen atom.

Furthermore, the functionalized silicone oils
10 obtained from processes using homogeneous catalysis are generally coloured, of the order of 120 to 300 hazen units, which for this reason limits their fields of use which can be envisaged, in particular in the field of transparent antiadhesive films for paper or for
15 transparent films (for example of polyester type). This colouring is generally due to the presence, in the functionalized oils, of metal aggregates or of colloids with a nanometric size derived from the homogeneous catalytic compositions used in the hydrosilylation
20 processes of the prior art. In these cases, the functionalized silicone oils require additional filtration and purification stages in order to be able to be useable after crosslinking in the field of transparent films; these additional stages make the
25 industrial implementation expensive and thus of little viability economically.

The Applicant Company has developed a novel

process for the preparation of functionalized silicone oils by hydrosilylation which makes it possible to significantly reduce isomerization reactions within the unsaturated synthon and, furthermore, to very substantially reduce, during the devolatilization stage, the opening of a ring including an oxygen atom present on the unsaturated synthon.

The process employed makes it possible to obtain transparent and translucent functionalized silicone oils, which makes it possible to use the silicone oils according to the invention in applications which require this property, without requiring additional filtration or purification stages.

In particular, the silicone oils obtained from the process of the invention can be used after crosslinking in the field of inks, in the field of varnishes and in the field of coatings, in particular films, which are transparent and/or antiadhesive, by applications to supports of highly varied natures; for example, papers, glasses, plastics and/or metals.

In addition, the oils prepared are stable on storage.

Furthermore, the oils obtained according to the invention are devoid of toxicity; this is because, due to employing a heterogeneous catalytic composition, virtually no metals are found in the said oils.

According to the hydrosilylation process of

the present invention, the polyorganohydrosiloxane is reacted with different or identical synthons comprising a hydrocarbon-comprising ring in which is included at least one oxygen atom. This reaction is carried out in the presence of a heterogeneous catalytic composition comprising a metal chosen from the group consisting of cobalt, rhodium, ruthenium, platinum, palladium and nickel deposited on an inert support. The metal of the catalytic composition is preferably platinum.

10 The amount of metal present in the heterogeneous catalytic composition is between 0.005% and 5% with respect to the weight of the inert support. This amount of metal is also between 1 and 1000 ppm with respect to the weight of the

15 polyorganohydrosiloxane.

By definition, heterogeneous catalytic composition is understood to mean a catalytic composition, which can be solid or liquid, which is not dissolved in the reaction mixture, i.e. the reaction

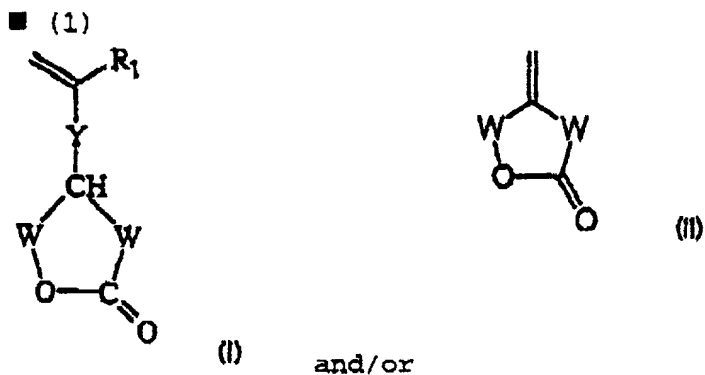
20 mixture comprises at least two phases, one of which is formed by the catalytic composition.

The metal is deposited on varied inert supports, such as carbon black, charcoal, alumina, treated or untreated silica, barium sulphate or

25 crosslinked silicones. The particle size of the catalytic supports is advantageously greater than 10 μm , in order to be able to be filtered well without

requiring filtration adjuvants. Thus, this particle size is such that it is possible to greatly reduce the filtration time.

The synthons comprise at least one hydrocarbon-comprising ring in which is included an oxygen atom and have the formula:



1 2

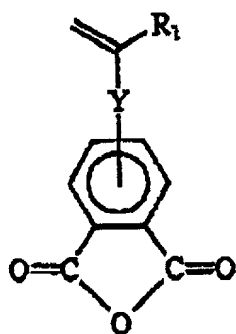
in which:

- 10 ■ the symbols W are identical or different and correspond to a divalent hydrocarbon-comprising radical chosen from linear or branched alkylene radicals having from 1 to 12 carbon atoms, it being possible for one of the symbols W to be a free valency;
- 15 ■ the symbol Y corresponds to a free valency or a divalent radical chosen from linear or branched alkylene radicals having from 1 to 12 carbon atoms which can comprise a heteroatom,
- 20

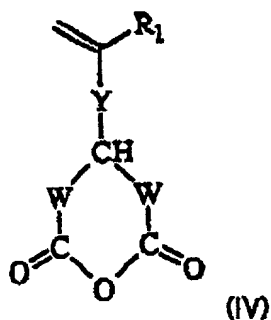
preferably an oxygen atom;

- the symbol R_1 corresponds to a hydrogen atom or monovalent hydrocarbon-comprising radical chosen from linear or branched alkyl radicals having from 1 to 12 carbon atoms and preferably a hydrogen atom or a methyl radical;

■ (2)



and/or



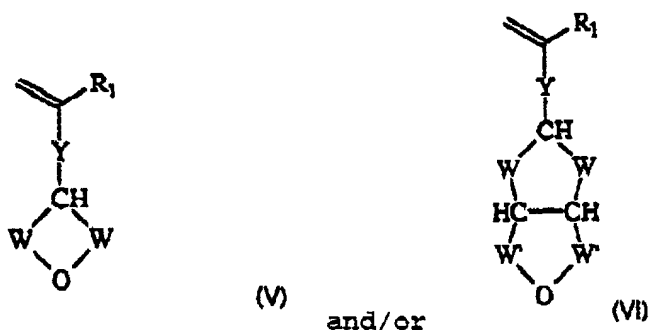
in which:

- the symbols W are identical or different and correspond to a divalent hydrocarbon-comprising radical chosen from linear or branched alkylene radicals having from 1 to 12 carbon atoms, it being possible for one of the symbols W to be a free valency;
- the symbol Y corresponds to a free valency or a divalent radical chosen from linear or branched alkylene radicals having from 1 to 12 carbon atoms which can comprise a heteroatom.

preferably an oxygen atom;

- the symbol R_1 corresponds to a hydrogen atom or monovalent hydrocarbon-comprising radical chosen from linear or branched alkyl radicals having from 1 to 12 carbon atoms and preferably a hydrogen atom or a methyl radical;

■ (3)

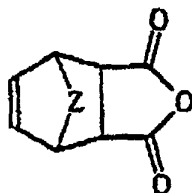


in which:

- the symbols W are identical or different and correspond to a divalent hydrocarbon-comprising radical chosen from linear or branched alkylene radicals having from 1 to 12 carbon atoms which can comprise at least one hydroxyl functional group, it being possible for one of the symbols W to be a free valency for (V) and it being possible for both symbols W simultaneously to be a free valency for (VI);

- 5
- the symbols W' are identical or different and correspond to a divalent hydrocarbon-comprising radical chosen from linear or branched alkylene radicals having from 1 to 12 carbon atoms, it being possible for at least one of the symbols W' to be a free valency;
 - 10 ■ the symbol Y corresponds to a free valency or a divalent radical chosen from linear or branched alkylene radicals having from 1 to 12 carbon atoms which can comprise a heteroatom, preferably an oxygen atom;
 - 15 ■ the symbol R_1 corresponds to a hydrogen atom or monovalent hydrocarbon-comprising radical chosen from linear or branched alkyl radicals having from 1 to 12 carbon atoms and preferably a
 - 20 hydrogen atom or a methyl radical; and

■ (4)



(VII)

in which:

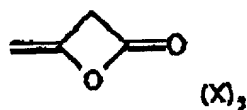
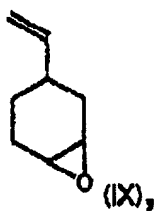
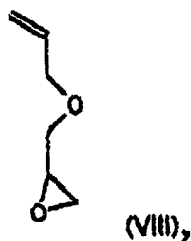
- the symbols W are identical or different

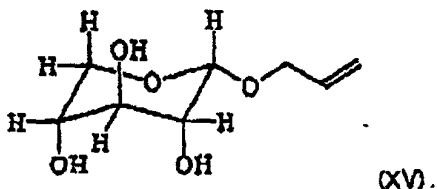
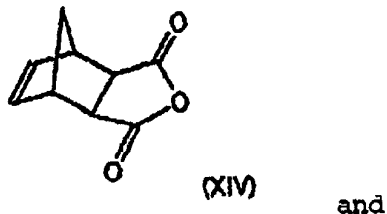
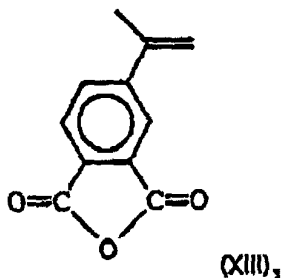
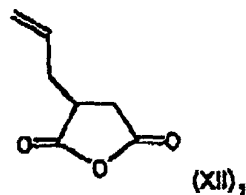
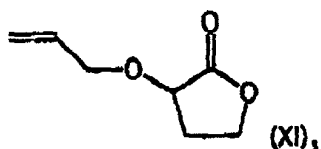
and correspond to a free valency or a
divalent hydrocarbon-comprising radical
chosen from linear or branched alkylene
radicals having from 1 to 2 carbon
atoms;

5

- the symbol Z corresponds to a divalent
radical chosen from a carbon atom or a
heteroatom.

The hydrocarbon-comprising ring in which is
included the oxygen atom preferably comprises at most 8
atoms in the said ring. Furthermore, the best results
in agreement with the hydrosilylation process of the
invention are obtained with synthons which only
comprise one hydrocarbon-comprising ring in which is
included an oxygen atom. In particular, the synthons
used which give good results (see examples below) have
the formula:





5

The synthons which react with the polyorganohydrosiloxane are generally identical synthons. The polyorganohydrosiloxane/synthons molar ratio is between 0.01 and 100, preferably between 0.1 and 10.

The polyorganohydrosiloxanes used in the processes according to the invention are very diverse in nature. These polyorganohydrosiloxanes can be linear or cyclic and have the mean formulae:

15



(XVI)

5

- 10

- 15

- 20

$$10 < a + b \leq 100;$$

■ c and d are integers or fractions, such that

$$- 0 < c < 5, \text{ preferably } 0 < c < 3,$$

$$- 1 < d < 10, \text{ preferably } 1 < d < 5,$$

$$- 3 < a + b < 10, \text{ preferably}$$

$$3 < a + b < 5.$$

In the context of the invention, various types of heterogeneous catalytic compositions can be used.

Use may be made, as non-limiting examples, of platinum on charcoal or carbon black, such as the catalytic composition comprising 2.5% by weight of platinum deposited on the CECA 2S support developed by the company Ceca, the SCAT 20 catalytic composition (1% Pt) from the company Engelhard or the 88 231 catalytic composition (1% Pt) from the company Heraeus. In this case, the platinum can be deposited on this type of support by deposition of chloroplatinic acid, followed by a neutralization and by a reduction. Likewise, the use of platinum on alumina, preferably of α type, such as the CAL 101 catalytic composition (0.3% Pt, SCS9 support composed of α -alumina) sold by the company Procatalyse or the 88 823 catalytic composition from the company Heraeus (0.5% Pt on α -alumina), gives good results.

The process according to the invention can be

carried out according to various alternative forms. In particular, it is possible to use a first implementation in which the combined reactants and catalytic composition are mixed in the reaction mixture (batch type). The second implementation of the process according to the invention can be continuous with a stationary bed of heterogeneous catalytic composition over which pass the polyorganohydrosiloxane to be functionalized and the synthon. This type of implementation is advantageous in the case where the size of the grains of the inert support of the catalytic composition is greater than 100 μm .

In the context of its experimental tests, the Applicant Company has developed an advantageous process in agreement with the first implementation. This process for hydrosilylation between a polyorganohydrosiloxane and an unsaturated synthon comprises the following stages:

(a) an amount of 5 to 5000 ppm, preferably of 10 to 100 ppm, of heterogeneous catalytic composition with respect to the total mass of the reactants is introduced under an inert gas into the reaction mixture;

(b) the synthon is introduced into the reaction mixture;

(c) the said mixture is heated to a temperature of between 25°C and 200°C and preferably

between 50°C and 160°C;

(d) the polyorganohydrosiloxane is subsequently introduced over a period of time of between 0 and 24 hours, preferably between 2.5 and 5 hours, the synthon/silicone molar ratio being between 1 and 1.10;

(e) the reaction mass is subsequently filtered in order to separate the heterogeneous catalytic composition and the functionalized silicone oil; and

(f) the functionalized silicone oil is finally devolatilized.

This advantageous process can be carried out in bulk, which means that the reaction between the polyorganohydrosiloxane and the synthon is carried out in the absence of solvent. However, numerous solvents, such as toluene, xylene, octamethyltetrasiloxane, cyclohexane or hexane, can be used.

Furthermore, the molar amount of synthon poured in during the stage (b) is less than that which is used for a conventional process of the prior art. The synthon/polyorganohydrosiloxane molar ratio is advantageously between 1 and 1.05, without harming the quality of the functionalized oils obtained and the reaction yield.

The filtration stage (e) makes it possible, if appropriate, to remove any remaining trace of

5 washing, and without a substantial fall in activity
with regard to its performance being recorded.

10 very stable and do not undergo changes during the
devolatilization stage. Their viscosities are very
substantially lower with respect to those of the oils
obtained from the same reactants and according to the
processes of the prior art, in particular those using
15 homogeneous catalysts.

20 reflects the absence of opening of the rings comprising an oxygen atom and thus the absence of polymerization reactions, including during the devolatilization, due to the opening of these rings.

25 obtained is stable on storage over a very long period
of time, which means that no side reaction takes place
in the said oils (no formation of gum and/or of resin

over time).

Furthermore, the oils prepared in agreement with the processes according to the invention are virtually transparent, with zero colouring and zero turbidity. This absence of colouring is apparent in particular with the catalytic compositions with an inert support composed of carbon black. In the context of our invention, zero colouring is understood to mean a colouring of less than 90 hazen units and preferably of less than 40 hazen units. A colouring of between 40 and 90 hazen units is observed solely in the case where the synthons are themselves coloured at the beginning before the hydrosilylation; the colouring is in no case due to the implementation of the process of the invention. If the synthons are colourless before reaction, the oils prepared have a colouring of less than 40 hazen units. As regards the turbidity, the oils are nonturbid when their turbidity is less than 1 NTU and/or only exhibit minimum traces of turbidity.

20 These oils also have a very low content of
metal resulting from the catalytic composition, which
very much limits the undesirable reactions which the
metal could cause if its content were higher. For
example, in the case of oils obtained according to the
25 invention in the presence of a catalytic composition
comprising in particular platinum, it is possible to
mix the said oils with other molecules comprising $\equiv\text{SiH}$

functional groups and molecules comprising unsaturated bonds without the risk of a further hydrosilylation reaction between these molecules.

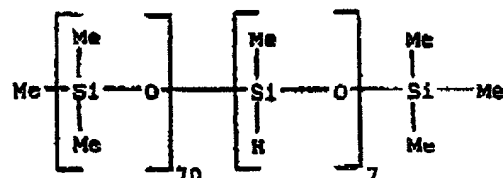
The level of epoxy quantitatively determined
5 in the oils obtained according to the invention is very high and the level of epoxy quantitatively determined/theoretical epoxy level ratio is between 0.95 and 1, this theoretical epoxy level corresponding to the level of $\equiv\text{SiH}$ quantitatively determined on the
10 polyorganohydrosiloxane before reaction.

The silicone oils according to the invention, because of their properties, are thus employed as additive (for example, as diluent) or as main component (for example, as resin) in the preparation of
15 crosslinkable compositions employed to prepare inks, varnishes and/or coatings which are transparent and colourless. These crosslinkable compositions generally comprise a photoinitiator and an organic and/or silicone resin with epoxy and/or acrylate
20 functionality; in addition, these compositions can comprise a diluent and/or a solvent. These compositions can be crosslinked as the case may be, for example under U.V. radiation and/or under an electron beam.

EXAMPLES

25 The examples below illustrate the preparation of functionalized silicone oils obtained according to the process of the present invention.

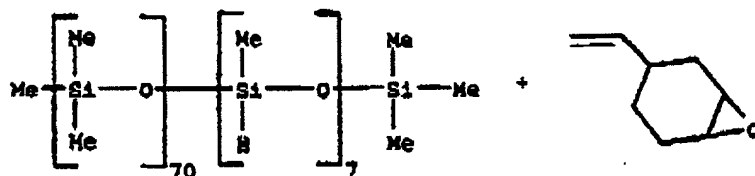
Examples 1 to 9 relate to the synthesis of silicone oils functionalized by 1,2-epoxy-4-vinylcyclohexane synthons with a polyorganohydrosiloxane for which the number of 5 milliequivalents of =SiH functional group is 128 per 100 g of polyorganohydrosiloxane and which has the mean formula (XVIII):

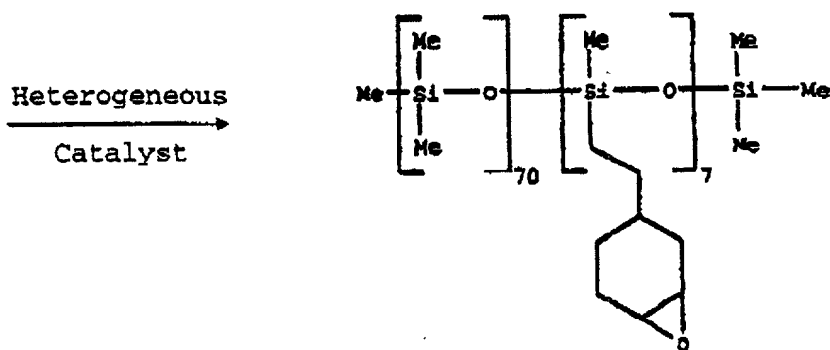


Examples 11 to 14 relate to the synthesis of 10 silicone oils functionalized by 1,2-epoxy-4-vinylcyclohexane synthons with a polyorganohydrosiloxane of mean formula (XVI) for which the values of X, a and b are specified in each example.

Examples 1 to 3 relate to preparations 15 according to the prior art and Examples 4 to 14 relate to preparations in agreement with the subject-matter of our invention.

The reaction scheme is as follows:





Quantitative determination of the $\equiv\text{SiH}$ groups present on the functionalized oils obtained is carried out by gas analysis. The amount of H_2 given off during the reaction between the functionalized silicone oil obtained and 1-butanol in the presence of potassium hydroxide as catalyst (2 g of KOH in 50 ml of 1-butanol) is measured.

The colouring of the functionalized oils obtained is measured with the help of an LTM1 liquid tester device from Dr. Lange using two beams for the measurement by transmission.

The turbidity of the functionalized oils obtained is measured with the help of a Haack turbidimeter by light dispersion (measurement by ratio).

The platinum content in the functionalized oils obtained is measured by ICP-MS.

The viscosity of the functionalized oils obtained is measured with the help of a Brookfield device according to the dynamic method (by shearing).

The quantitative determination of the epoxy groups on the functionalized oils obtained is measured with the help of a potentiometric device of 716 DMS Titrino type from Metrohm according to the method of I.M. Kolthoff and P.J. Elving (Treatise on Analytical Chemistry, Part II, Vol. 14, p. 288).

Example 1:

6.07 μ l of Karstedt homogeneous catalytic composition comprising 11.6% Pt (11.6 ppm of Pt in the mixture) and 8.68 g (69.89 mmol, 5% excess) of 1,2-epoxy-4-vinylcyclohexane were introduced under argon into a 100 ml three-necked flask equipped with a vertical stirrer, a reflux condenser, a thermometer and a septum.

This mixture is heated to 90°C. 52 g (66.56 mmol) of polyorganohydrosiloxane of formula (XVIII) are then run in over a period of 1 hour.

After the reactant has been run in, the degree of conversion of SiH is 99.7%.

After devolatilization at 90°C for 2 hours, a functionalized oil is recovered which has a viscosity of 930 mPa.s.

The colouring of the oil is 240 hazen units and the platinum content is 11.6 ppm.

The level of epoxy quantitatively determined/theoretical epoxy level ratio is 0.91.

Example 2:

6.07 μ l of Karstedt homogeneous catalytic composition comprising 11.6% Pt (11.6 ppm of Pt in the mixture) and 8.68 g (69.89 mmol, 5% excess) of 1,2-epoxy-4-vinylcyclohexane were introduced under argon into a 100 ml three-necked flask equipped with a vertical stirrer, a reflux condenser, a thermometer and a septum.

The mixture is heated to 90°C. 52 g (66.56 mmol) of polyorganohydrosiloxane of formula (XVIII) are then run in over a period of 1 hour.

After the reactant has been run in, the degree of conversion of SiH is 99.7%.

Heating is continued for 3 hours. After filtration, the oil is devolatilized at 120°C for 2 hours.

The functionalized oil obtained is crosslinked and exists in solid form.

Example 3:

175 mg of milled heterogeneous catalyst comprising 1% Pt on a support composed of TiO_2 , 16.7 g of toluene and 2.5 g (20.2 mmol) of 1,2-epoxy-4-vinylcyclohexane were introduced under argon into a 100 ml three-necked flask equipped with a vertical stirrer, a reflux condenser, a thermometer and a septum.

The mixture is heated to 90°C. 15 g of

polyorganohydrosiloxane of formula (XVIII) are then run in over a period of 3 hours.

After the reactant has been run in, the degree of conversion is 91.7%. 2 hours later, the degree is 96.6% and then reaches 97.4% 20 hours after the reactant has been run in.

The reaction mixture is filtered on a Eurofiltrec R3506 filter under a pressure of 3.5×10^5 Pa.

10 The oil obtained is then devolatilized using a rotary evaporator at 100°C under a vacuum of 2×10^2 Pa.

A functionalized oil is recovered which is highly coloured, of the order of 2430 hazen units, 15 which has a platinum content of 8.1 ppm and which has a viscosity of 1460 mPa·s. The level of epoxy quantitatively determined/calculated epoxy level ratio is 0.91.

Example 4:

20 3.89 g of non-milled heterogeneous catalytic composition of CAL 101 type (100 ppm of Pt in the mixture) and 16.7 g (0.134 mol, 5% excess) of 1,2-epoxy-4-vinylcyclohexane were introduced under argon into a 250 ml three-necked flask equipped with a 25 vertical stirrer, a reflux condenser, a thermometer and a septum.

The mixture is heated to 90°C . 100 g

(0.128 mol) of polyorganohydrosiloxane of formula (XVIII) are then run in over a period of 3 hours.

After the reactant has been run in, the degree of conversion of SiH is 98.6%. 2 hours after the
5 reactant has been run in, the degree of conversion is 100%.

The reaction mass is filtered through sintered glass with a clarcel precoat. Devolatilization is carried out using a rotary evaporator at 100°C under
10 a vacuum of 2×10^2 Pa for 2 hours.

A perfectly transparent functionalized oil is recovered (colouring of the order of 83 hazen units and no turbidity). The viscosity measured is 290 mPa·s and the platinum content is 2.1 ppm. After storing for 3
15 months (at room temperature and under nitrogen), the viscosity is found to be identical.

The level of epoxy quantitatively determined/calculated epoxy level ratio is 0.96.

Example 5:

20 4.668 g of heterogeneous catalytic composition comprising 2.5% Pt on a CECA 2S support (100 ppm of Pt) and 166.9 g (1.344 mol, 5% excess) of 1,2-epoxy-4-vinylcyclohexane were introduced under argon into a 2 litre three-necked flask equipped with a
25 vertical stirrer, a reflux condenser, a thermometer and a septum.

The mixture is heated to 90°C. 1 kg

(1.28 mol) of polyorganohydrosiloxane of formula (XVIII) is run in over a period of 3 hours.

After the reactant has been run in, the degree of conversion of SiH is 96.4% and this reaches 5 97.5% after 2 hours and then 99.7% after 5 hours.

After filtration, devolatilization is carried out using a rotary evaporator at 100°C under a vacuum of 2×10^2 Pa.

A functionalized oil is recovered which has a 10 viscosity of 300 mPa·s. After storing for 3 months (at room temperature and under nitrogen), the viscosity is found to be identical.

The colouring is 45 hazen units and the platinum content is less than 0.16 ppm. The level of 15 epoxy quantitatively determined/calculated epoxy level ratio is 0.96. No turbidity observed.

Example 6:

All the washed, dried and recovered heterogeneous catalytic composition from Example 5 and 20 16.7 g (0.1344 mol, 5% excess) of 1,2-epoxy-4-vinylcyclohexane were introduced under argon into a 250 ml three-necked flask equipped with a vertical stirrer, a reflux condenser, a thermometer and a septum.

25 The mixture is heated to 90°C. 100 g (0.128 mol) of polyorganohydrosiloxane of formula (XVIII) are run in over a period of 3 hours.

After the reactant has been run in, the degree of conversion of SiH is 87.0%. 2 hours after the reactant has been run in, the degree reaches 94.6%, then 95% 8 hours after and 96.2% 24 hours after.

5 The reaction mass is filtered through sintered glass with a clarcel precoat. Devolatilization is carried out using a rotary evaporator at 100°C under a vacuum of 2×10^2 Pa for 2 hours.

A functionalized oil is recovered which has a
10 viscosity of 270 mPa·s. After storing for 3 months (at room temperature and under nitrogen), the viscosity is found to be identical.

The colouring is 35 hazen units and the platinum content is less than 0.15 ppm.

15 The level of epoxy quantitatively determined/calculated epoxy level ratio is 0.92.

Turbidity is not observed.

Example 7:

0.360 g of heterogeneous catalytic
20 composition comprising 2.5% Pt on a CECA 2S support and 13.9 g (0.112 mol, 5% excess) of 1,2-epoxy-4-vinylcyclohexane were introduced under argon into a 100 ml three-necked flask equipped with a vertical stirrer, a reflux condenser, a thermometer and a
25 septum. The mixture is heated to 90°C. 90 g (0.107 eq.) of polyorganohydrosiloxane of formula

(XVIII) are run in over a period of 3 hours.

After the reactant has been run in, the degree of conversion of SiH is 90.3% and this reaches 99.1% 8 hours later.

- 5 After filtration, devolatilization is carried out at 120°C under a vacuum of 2×10^2 Pa for 2 hours.

A functionalized oil is recovered which has a viscosity of 320 mPa·s. After storing for 3 months (at room temperature and under nitrogen), the viscosity is
10 found to be identical.

The colouring is 25 hazen units and the platinum content is less than 0.17 ppm.

The level of epoxy quantitatively determined/calculated epoxy level ratio is 0.96.

- 15 No turbidity observed.

Example 8:

0.233 g of heterogeneous catalytic composition (5% Pt on a support composed of barium sulphate) from the company Heraeus (100 ppm of Pt in
20 the mixture) and 16.7 g (0.1344 mol, 5% excess) of 1,2-epoxy-4-vinylcyclohexane were introduced under argon into a 250 ml three-necked flask equipped with a vertical stirrer, a reflux condenser, a thermometer and a septum.

- 25 The mixture is heated to 90°C. 100 g (0.128 mol) of polyorganohydrosiloxane of formula (XVIII) are then run in over a period of 3 hours.

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After the reactant has been run in, the degree of conversion of SiH is 63.3%. 2 hours after the reactant has been run in, this degree reaches 91.4% and 93.8% 5 hours after the reactant has been run in. 24 5 hours after, the degree of conversion is 93.1%.

Devolatilization is carried out using a rotary evaporator at 100°C under a pressure of 2×10^2 Pa for 2 hours.

A functionalized oil is recovered which has a 10 viscosity of 280 mPa·s. After storing for 3 months (at room temperature and under nitrogen), the viscosity is found to be identical.

The colouring is 57 hazen units and the platinum content is less than 4.5 ppm.

15 The level of epoxy quantitatively determined/calculated epoxy level ratio is 0.96.

No turbidity observed.

Example 9:

7.78 g of unmilled heterogeneous catalytic 20 composition of CAL 101 type (100 ppm of Pt in the mixture) are introduced into a U-shaped tube equipped with a thermometer and flushing is carried out with argon.

33.4 g of 1,2-epoxy-4-vinylcyclohexane 25 (0.2688 mol, 5% excess) are introduced into a 500 ml three-necked flask connected to the U-shaped tube. The 1,2-epoxy-4-vinylcyclohexane passes into the U-shaped

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tube containing the catalytic composition (peristaltic pump with rate = 100 ml/min) and then returns to the round-bottomed flask.

The reaction mixture is heated to 90°C. 200 g of polyorganohydrosiloxane of formula (XVIII) are then run into the three-necked flask over a period of 3 hours. The polyorganohydrosiloxane and 1,2-epoxy-4-vinylcyclohexane mixture is subsequently passed over the catalytic composition.

After the reactant has been run in, the degree of conversion of the SiH units is 94.8% and, 2 hours after this, the degree reaches 98.4% to ultimately reach 100%.

The reaction mixture is filtered through sintered glass with a clarcel precoat. Devolatilization is carried out using a rotary evaporator at 100°C under a vacuum of 2×10^2 Pa for 2 hours.

A functionalized oil is recovered which has a viscosity of 280 mPa·s. After storing for 3 months (at room temperature and under nitrogen), the viscosity is found to be identical.

The colouring is 114 hazen units and the platinum content is 2.9 ppm.

The level of epoxy quantitatively determined/calculated epoxy level ratio is 0.97.

No turbidity observed.

The catalytic composition is recovered and

washed with toluene as soon as the reaction is complete (8 h after the reactant has begun to be run in) and then it is dried with a stream of argon.

Example 10:

5 All the washed and dried heterogeneous catalytic composition of CAL 101 type recovered from Example 9 is introduced into a U-shaped tube equipped with a thermometer and then the assembly is conditioned under argon.

10 33.4 g of 1,2-epoxy-4-vinylcyclohexane (0.2688 mol, 5% excess) are charged to a 500 ml three-necked flask. The 1,2-epoxy-4-vinylcyclohexane is passed over the catalytic composition contained in the U-shaped tube and then returns to the round-bottomed
15 flask (under the action of a peristaltic pump with rate = 100 ml/min).

The reaction mixture is heated to 90°C. 200 g of polyorganohydrosiloxane of formula (XVIII) are subsequently run in over a period of 3 hours. The
20 mixture of polyorganohydrosiloxane of formula (XVIII) and of 1,2-epoxy-4-vinylcyclohexane is subsequently passed over the catalytic composition (under the action of a pump).

After the reactant has been run in, the
25 degree of conversion of the SiH units is 92.4%. 2 hours after this operation of running in the reactant has finished, the degree of conversion is 94.1% and then, 8

hours after, this level reaches 95.4%.

The reaction mass is filtered through sintered glass with a clarcel precoat. Devolatilization is carried out using a rotary evaporator at 100°C under
5 a pressure of 2×10^2 Pa for 2 hours.

A functionalized oil is recovered which has a viscosity of 270 mPa.s. After storing for 3 months (at room temperature and under nitrogen), the viscosity is found to be identical.

10 The modified silicone oil obtained is transparent; its colouring is 83 hazen units and the platinum content is 2.1 ppm.

The level of epoxy quantitatively determined/calculated epoxy level ratio is 0.92.

15 No turbidity observed.

Example 11:

2.045 g of heterogeneous catalytic composition comprising 3% Pt on a dried black charcoal support, with the commercial reference 7075 from
20 Engelhard, and 13.46 g (0.108 mol, 5% excess) of 1,2-epoxy-4-vinylcyclohexane were introduced under argon into a two litre four-necked flask equipped with a vertical stirrer, a reflux condenser, a thermometer and a septum cap.

25 The mixture is heated to 100°C. 600 g (0.103 eq.) of polyorganohydrosiloxane of formula (XVI), in which $X = CH_3$, $a = 225$ and $b = 2$, are run in

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over a period of 2 hours.

After the reactant has been run in, the degree of conversion of SiH is 64.5%. After 23 hours, it is 83.3%. After heating to 120°C, the degree of conversion of SiH is 100% after 5 days.

After filtration, devolatilization is carried out at 120°C under a vacuum of 1×10^2 Pa for 5 hours.

A functionalized oil is recovered which has a viscosity of 610 mPa·s. This viscosity is found to be unchanged after storing for three months at room temperature under nitrogen.

The colouring is 30 hazen units and the platinum content is less than 0.11 ppm.

Turbidity is not observed.

15 Example 12:

2.55 g of heterogeneous catalytic composition comprising 2.5% Pt on a CECA 2S support comprising 52% by mass of water and 2049 g (16.5 mol, 10% excess) of 1,2-epoxy-4-vinylcyclohexane were introduced under argon into a 3.5 litre reactor equipped with a vertical stirrer, a reflux condenser, a dip pipe, a thermometer and a septum cap.

The mixture is heated to 110°C. 1007 g (15 eq.) of polyorganohydrosiloxane of formula (XVI), in which $X = H$, $a = 1$ and $b = 0$, are run in over a period of five hours via the dip pipe.

After the reactant has been run in, the

degree of conversion of SiH is 99.98%.

After filtration, devolatilization is carried out at 120°C under a vacuum of less than 1×10^2 Pa for 10 h.

5 A functionalized oil is recovered which has a viscosity of 51.3 mPa·s. This viscosity is unchanged after storing for three months at room temperature under nitrogen.

 The colouring is 30 hazen units and the
10 platinum content is less than 0.11 ppm.

Turbidity is not observed (0.2 NTU).

Example 13:

 3.74 g of heterogeneous catalytic composition comprising 2.5% Pt on a dried CECA 2S support and
15 433.85 g (3.8 mol, 5% excess) of allyl glycidyl ether were introduced under argon into a two litre four-necked flask equipped with a vertical stirrer, a reflux condenser, a thermometer and a septum cap.

 The mixture is heated to 130°C. 500 g
20 (3.62 eq.) of polyorganohydrosiloxane of formula (XVI), in which $X = H$, $a = 9$ and $b = 4.5$, are run in over a period of 5 hours.

 After the reactant has been run in, the degree of conversion of SiH is 92.7%. After 10 hours,
25 it is 99.8%.

 After filtration, devolatilization is carried out at 120°C under a vacuum of 1×10^2 Pa for 5 hours.

A functionalized oil is recovered which has a viscosity of 62 mPa·s. This viscosity is unchanged after storing for three months at room temperature under nitrogen.

- 5 The colouring is 25 hazen units and the platinum content is less than 0.18 ppm.

Turbidity is not observed.

Example 14:

- 3.06 g of heterogeneous catalytic composition
10 comprising 3% Pt on a dried black charcoal support, of reference 7075 from the company Engelhard, 20 g of p-xylene and 6.74 g (41 mmol, 10% excess) of nadic anhydride were introduced under argon into a 100 ml four-necked flask equipped with a vertical stirrer, a
15 reflux condenser, a thermometer and a septum cap.

The mixture is heated to 120°C. 10 g (37.3 meq.) of polyorganohydrosiloxane of formula (XVI), in which $X = CH_3$, $a = 9.1$ and $b = 4$, are run in over a period of two hours.

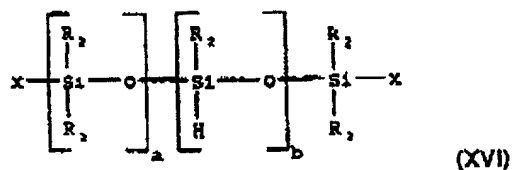
- 20 After 24 hours, the degree of conversion is 41.7% and then 92.4% after 72 hours, 98.9% after 96 hours and 99.7% after 120 hours.

After filtration, devolatilization is carried out, after a temperature rise over two hours, at 120°C
25 under a vacuum of 1×10^2 Pa for 5 hours.

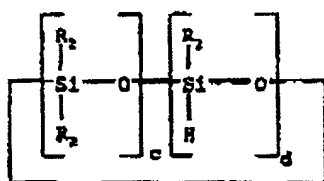
A colourless functionalized oil is recovered.

CLAIMS

1. Process for the preparation of a nonturbid functionalized silicone oil of stable viscosity by hydrosilylation of a polyorganohydrosiloxane with synthons, characterized in that:
- (1) the synthons hydrosilylated with the polyorganohydrosiloxane are different or identical, comprising at least one hydrocarbon-comprising ring in which is included at least one oxygen atom,
- (2) the said hydrosilylation reaction is carried out in the presence of a heterogeneous catalytic composition comprising a metal chosen from the group consisting of cobalt, rhodium, ruthenium, platinum and nickel deposited on an inert support, the said inert support being selected from the group consisting of carbon black, charcoal, alumina, silicate and barium oxide, and
- (3) the polyorganohydrosiloxane is linear or cyclic and has the mean formulae:



and/or



(XVII)

in which:

- the symbols R_2 are identical or different and correspond to a monovalent hydrocarbon-comprising radical chosen from the phenyl radical and linear or branched alkyl radicals having from 1 to 6 carbon atoms, preferably 1 to 3 carbon atoms;
- the symbols X are identical or different and correspond to a monovalent radical chosen from R_2 , a hydrogen atom, a methoxy radical and an ethoxy radical;
- a and b are integers or fractions, such that:
 - $0 < a \leq 200$, preferably $0 < a \leq 99$,
 - $0 \leq b \leq 200$, preferably $1 < b \leq 100$,
 - and at least one of the two X groups corresponds to the hydrogen radical if $b = 0$,
 - $5 < a + b \leq 200$, preferably $10 < a + b \leq 100$;
- c and d are integers or fractions, such that:
 - $0 < c < 5$, preferably $0 < c < 3$,

- $1 < d < 10$, preferably $1 < d < 5$,

- $3 < a + b < 10$, preferably

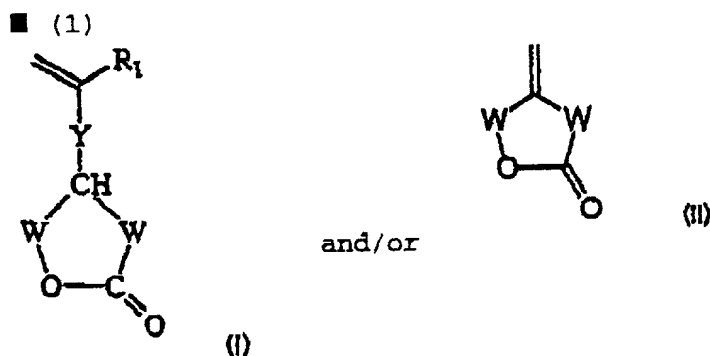
$3 < a + b < 5$.

2. Preparation process according to claim

5 1, characterized in that the functionalized oils obtained are colourless and prepared in the presence of a catalytic composition according to claim 1, the inert support for which is carbon black.

3. Process according to claim 1 or 2,

10 characterized in that the synthons comprise at least one hydrocarbon-comprising ring in which is included an oxygen atom, the synthons having the formula:



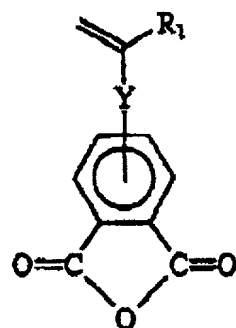
in which:

15 ■ the symbols W are identical or different and correspond to a divalent hydrocarbon-comprising radical chosen from linear or branched alkylene radicals having from 1 to 12 carbon

20 atoms, it being possible for one of the symbols W to be a free valency;

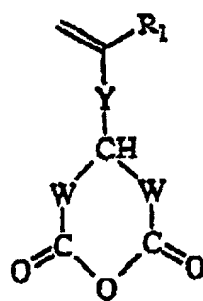
- the symbol Y corresponds to a free valency or a divalent radical chosen from linear or branched alkylene radicals having from 1 to 12 carbon atoms which can comprise a heteroatom, preferably an oxygen atom;
- the symbol R₁ corresponds to a hydrogen atom or monovalent hydrocarbon-comprising radical chosen from linear or branched alkyl radicals having from 1 to 12 carbon atoms and preferably a hydrogen atom or a methyl radical;

■ (2)



(III)

and/or



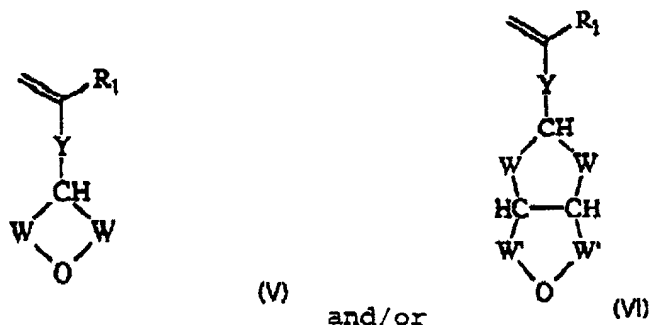
(IV)

in which:

- the symbols W are identical or different and correspond to a divalent hydrocarbon-comprising radical chosen from linear or branched alkylene radicals having from 1 to 12 carbon atoms, it being possible for one of the symbols W to be a free valency;

- the symbol Y corresponds to a free valency or a divalent radical chosen from linear or branched alkylene radicals having from 1 to 12 carbon atoms which can comprise a heteroatom, preferably an oxygen atom;
- the symbol R₁ corresponds to a hydrogen atom or monovalent hydrocarbon-comprising radical chosen from linear or branched alkyl radicals having from 1 to 12 carbon atoms and preferably a hydrogen atom or a methyl radical;

■ (3)



in which:

- the symbols W are identical or different and correspond to a divalent hydrocarbon-comprising radical chosen from linear or branched alkylene radicals having from 1 to 12 carbon atoms which can comprise at least one hydroxyl functional group, it being

possible for one of the symbols W to be
a free valency for (V) and it being
possible for both symbols W
simultaneously to be a free valency for
(VI);

5

- the symbols W' are identical or
different and correspond to a divalent
hydrocarbon-comprising radical chosen
from linear or branched alkylene
radicals having from 1 to 12 carbon
atoms, it being possible for at least
one of the symbols W' to be a free
valency;

10

- the symbol Y corresponds to a free
valency or a divalent radical chosen
from linear or branched alkylene
radicals having from 1 to 12 carbon
atoms which can comprise a heteroatom,
preferably an oxygen atom;

15

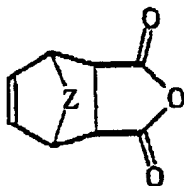
- the symbol R₁ corresponds to a hydrogen
atom or monovalent hydrocarbon-
comprising radical chosen from linear or
branched alkyl radicals having from 1 to
12 carbon atoms and preferably a
hydrogen atom or a methyl radical; and

20

25

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■ (4)



(VII)

in which:

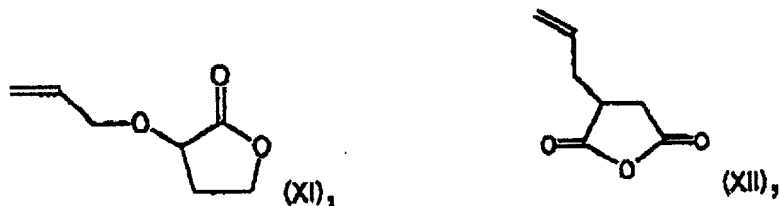
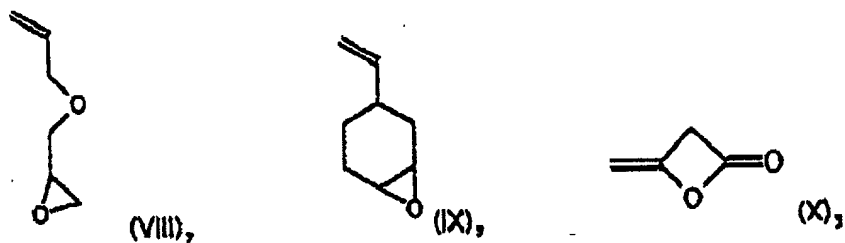
■ the symbols W are identical or different
 5 and correspond to a free valency or a
 divalent hydrocarbon-comprising radical
 chosen from linear or branched alkylene
 radicals having from 1 to 2 carbon
 atoms;

10 ■ the symbol Z corresponds to a divalent
 radical chosen from a carbon atom or a
 heteroatom.

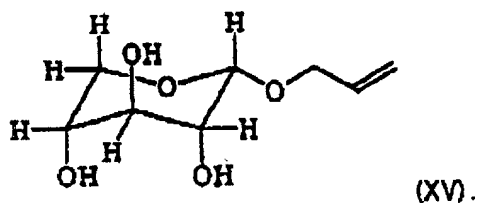
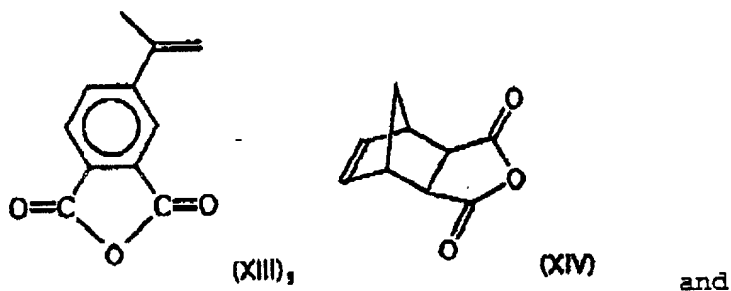
4. Process according to claim 3,
 characterized in that the hydrocarbon-comprising ring
 15 of the synthons comprises at most 8 atoms in the said
 ring.

5. Process according to either one of
 Claims 3 and 4, characterized in that the synthons
 comprise a hydrocarbon-comprising ring in which is
 20 included an oxygen atom.

6. Process according to any one of claims
 3, 4 and 5, characterized in that the synthon has the
 formula:



5



10

7. Process according to any one of claims 3 to 6, characterized in that the synthons which react with the polyorganohydrosiloxane are identical synthons.

8. Process according to any one of claims 1

to 7, characterized in that the polyorganohydro-siloxane/synthons molar ratio is between 0.01 and 100, preferably between 0.1 and 10.

9. Process according to either one of
5 claims 1 and 2, characterized in that the amount of metal is between 0.1% and 5% with respect to the weight of the inert support.

10. Process according to either one of
claims 1 and 2, characterized in that the amount of
10 metal in the catalytic composition is between 1 and 1000 ppm with respect to the weight of the polyorganohydrosiloxane.

11. Process according to either one of
claims 1 and 2, characterized in that the metal of the
15 catalytic composition is platinum.

12. Process according to any one of the preceding claims, characterized in that the polyorgano-hydrosiloxane and the synthon pass over or through a stationary bed of the catalytic composition.

20 13. Silicone oil comprising synthons comprising a hydrocarbon-comprising ring in which is included an oxygen atom, which can be obtained by the process according to any one of claims 1 to 12.

14. Silicone oil comprising synthons
25 comprising at least one epoxide, which can be obtained by the process according to any one of claims 1 to 12.

15. Silicone oil comprising synthons of

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formula (IX), which can be obtained by the process according to any one of claims 1 to 12.

16. Use of the silicone oils according to any one of claims 13, 14 and 15 in the preparation of antiadhesion products for paper, glass, plastic and/or metal.

17. Use of the silicone oils according to any one of claims 13, 14 and 15 in the preparation of varnishes, inks and/or coatings.

18. Process according to any one of claims 1 to 12, characterized in that it comprises the following stages:

- (a) an amount of 5 to 5000 ppm, preferably of 10 to 100 ppm, of heterogeneous catalytic composition with respect to the total mass of the reactants is introduced under an inert gas into the reaction mixture;
- (b) the synthon is introduced into the reaction mixture;
- (c) the said mixture is heated to a temperature of between 25°C and 200°C and preferably between 50°C and 160°C;
- (d) the polyorganohydrosiloxane is subsequently introduced over a period of time of between 0 and 24 hours, preferably between 2.5 and 5 hours, the synthon/polyorganohydrosiloxane molar ratio being between 1 and 1.10;

- (e) the reaction mass is subsequently filtered in order to separate the heterogeneous catalytic composition and the functionalized silicone oil; and
- 5 (f) the functionalized silicone oil is finally devolatilized.

19. Process according to claim 18, characterized in that the polyorganohydrosiloxane and the synthon react in the reaction mixture in the
10 absence of solvent.

20. Use of a supported heterogeneous catalytic composition in the preparation of functionalized silicone oils which are stable and nonturbid, characterized in that the heterogeneous
15 catalytic composition comprises a metal chosen from the group consisting of cobalt, rhodium, ruthenium, platinum and nickel deposited on an inert support, the said inert support being selected from the group consisting of carbon black, charcoal, alumina, silicate
20 and barium oxide and preferably carbon black.

21. Use according to claim 20 in the preparation of functionalized silicone oils which are stable, non-coloured and nonturbid, characterized in that the inert support of the heterogeneous catalytic
25 composition is carbon black.

COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY
 (Includes Reference to Provisional and PCT International Applications)

ATTORNEY'S DOCKET NUMBER

022701-803

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name;

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

METHOD FOR PREPARING SILICONE OILS BY HYDROSILYLATION WITH

POLYORGANOHYDROGENOSILOXANES AND UNITS CONTAINING AT LEAST ONE HYDROCARBON

the specification of which (check only one item below):

☐ is attached hereto.

☐ was filed as United States application

Number _____

on _____

and was amended

on _____ (if applicable).

☒ was filed as PCT international application

Number PCT/FR97/01055

on 12 June 1997

and was amended under PCT Article 19

on _____ (if applicable).

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose to the Office all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, §1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, §119 (a)-(e) of any foreign application(s) for patent or inventor's certificate or of any PCT international application(s) designating at least one country other than the United States of America listed below and have also identified below any foreign application(s) for patent or inventor's certificate or any PCT international application(s) designating at least one country other than the United States of America filed by me on the same subject matter having a filing date before that of the application(s) of which priority is claimed:

PRIOR FOREIGN/PCT APPLICATION(S) AND ANY PRIORITY CLAIMS UNDER 35 U.S.C. §119:

COUNTRY (if PCT, indicate "PCT")	APPLICATION NUMBER	DATE OF FILING (day, month, year)	PRIORITY CLAIMED UNDER 35 U.S.C. §119
FR	96/07272	12 June 1996	<u>X</u> Yes ___ No
			___ Yes ___ No
			___ Yes ___ No
			___ Yes ___ No
			___ Yes ___ No

I hereby claim the benefit under Title 35, United States Code § 119(e) of any United States provisional application(s) listed below.

(Application Number)

(Filing Date)

(Application Number)

(Filing Date)

COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY (CONTINUED)
(Includes Reference to Provisional and PCT International Applications)

ATTORNEY'S DOCKET NO.

022701-803

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) or PCT international application(s) designating the United States of America that is/are listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in that/those prior application(s) in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose to the Office all information known to me to be material to the patentability as defined in Title 37, Code of Federal Regulations §1.56, which became available between the filing date of the prior application(s) and the national or PCT international filing date of this application:

PRIOR U.S. APPLICATIONS OR PCT INTERNATIONAL APPLICATIONS DESIGNATING THE U.S. FOR BENEFIT UNDER 35 U.S.C. 120:

U.S. APPLICATIONS

STATUS (check one)

U.S. APPLICATION NUMBER

U.S. FILING DATE

PATENTED

PENDING

ABANDONED

PCT APPLICATIONS DESIGNATING THE U.S.

PCT APPLICATION NO.

PCT FILING DATE

U.S. APPLICATION NUMBERS
ASSIGNED (if any)

I hereby appoint the following attorneys and agent(s) to prosecute said application and to transact all business in the Patent and Trademark Office connected therewith and to file, prosecute and to transact all business in connection with international applications directed to said invention:

William L. Mathis 17,337
Peter H. Smolka 15,913
Robert S. Swecker 19,885
Platon N. Mandros 22,124
Benton S. Duffett, Jr. 22,030
Norman H. Stepno 22,716
Ronald L. Grudziecki 24,970
Frederick G. Michaud, Jr. 26,003
Alan E. Kopecki 25,813
Regis E. Slutter 26,999
Samuel C. Miller, III 27,360
Ralph L. Freeland, Jr. 16,110
Robert G. Mukai 28,531

George A. Hovanec, Jr. 28,223
James A. LaBarre 28,632
E. Joseph Gess 28,510
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Eric H. Weisblatt 30,505
James W. Peterson 26,057
Teresa Stanek Rea 30,427
Robert E. Krebs 25,885
William C. Rowland 30,888
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Patrick C. Keane 32,858
Bruce J. Boggs, Jr. 32,344
William H. Benz 25,952

Peter K. Skiff 31,917
Richard J. McGrath 29,195
Matthew L. Schneider 32,814
Michael G. Savage 32,596
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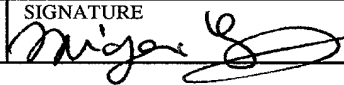
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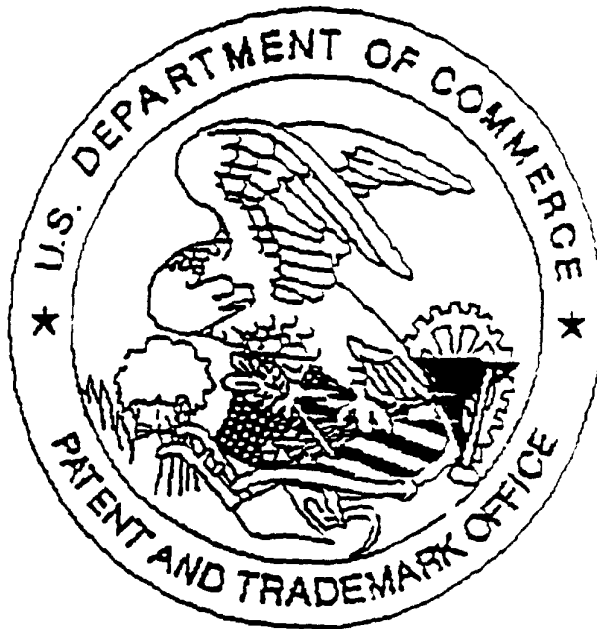
Norman H. Stepno
BURNS, DOANE, SWECKER & MATHIS, L.L.P.
P.O. Box 1404
Alexandria, Virginia 22313-1404

Address all telephone calls to: Norman H. Stepno at (703) 836-6620.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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RESIDENCE Les Hauts de Vienne, F-38200 Vienne, France		DATE January 25, 1999	
POST OFFICE ADDRESS Les Hauts de Vienne, F-38200 Vienne, France		CITIZENSHIP Germany	
FULL NAME OF SECOND JOINT INVENTOR, IF ANY Gérard MIGNANI		SIGNATURE 	
RESIDENCE 2, avenue des Freres Lumiere, F-69008 Lyon, France		DATE January 23, 1999	
POST OFFICE ADDRESS 2, avenue des Freres Lumiere, F-69008 Lyon, France		CITIZENSHIP France	
FULL NAME OF THIRD JOINT INVENTOR, IF ANY		SIGNATURE	
RESIDENCE		DATE	
CITIZENSHIP		POST OFFICE ADDRESS	
FULL NAME OF FOURTH JOINT INVENTOR, IF ANY		SIGNATURE	
RESIDENCE		DATE	
CITIZENSHIP		POST OFFICE ADDRESS	
FULL NAME OF FIFTH JOINT INVENTOR, IF ANY		SIGNATURE	
RESIDENCE		DATE	
CITIZENSHIP		POST OFFICE ADDRESS	
FULL NAME OF SIXTH JOINT INVENTOR, IF ANY		SIGNATURE	
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FULL NAME OF SEVENTH JOINT INVENTOR, IF ANY		SIGNATURE	
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FULL NAME OF EIGHTH JOINT INVENTOR, IF ANY		SIGNATURE	
RESIDENCE		DATE	
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